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Long-term Fuel Specific NO_x and Particle Emission Trends for In-Use Heavy-Duty Vehicles in California

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Abstract

Two California heavy-duty fleets have been measured in 2013, 2015 and 2017 using the On-road Heavy-duty Measurement System. The Port of Los Angeles drayage fleet has increased in age by 3.3 model years (4.2 to 7.5 years old) since 2013, with little fleet turnover. Large increases in fuel specific particle emissions (PM) observed in 2015 were reversed in 2017, returning to near 2013 levels, suggesting repairs and or removal of high emitting vehicles. Fuel specific oxides of nitrogen (NO_x) emissions of this fleet have increased and NO_x after-treatment systems do not appear to perform ideally in this setting. At Cottonwood weigh station in northern California, the fleet age has declined (7.8 to 6 years old) since 2013 due to fleet turnover significantly lowering the average fuel specific emissions for PM (-87%), black carbon (-76%) and particle number (-64%). Installations of retrofit-diesel particulate filters in 2007 and older vehicles have further decreased particle emissions. Cottonwood fleet fuel specific NO_x emissions have decreased slightly (-8%) during this period, however, newer technology vehicles with selective catalytic reduction systems (SCR) promise an additional factor of 4 to 5 further reductions in the long-haul fleet emissions as California transitions to an all SCR equipped fleet.

Introduction

Nitrogen oxides (NO_x = NO + NO_2) and particulate matter (PM) are major constituents of diesel exhaust from heavy-duty vehicles (HDVs). Because of this, HDVs' NO_x and PM emissions have been heavily regulated in the U.S., as they contribute to the formation of ozone and acid rain, are climate forcers, specifically black carbon (BC), and can lead to damaging health effects.[1-4] The most recent Federal and California NO_x and PM standards required an order of magnitude reduction to 0.2 and 0.01 g/bhp-hr, respectively. All HDV engines manufactured beginning in 2007 are required to comply with the PM standards and the NO_x requirements have undergone a phase-in beginning with 2010 engines.[5-8] In order to meet these low levels for NO_x and PM emissions, engine manufactures have implemented after-treatment systems that reduce NO_x via selective catalytic reduction systems (SCRs) and have also installed diesel particulate filters (DPFs) to trap PM before it is emitted into the atmosphere.[9]

SCRs utilize thermalized urea to reduce NO_x to nitrogen (N_2) and water, and reductions have been reported between 75 and 95 percent for tailpipe NO_x under optimal temperature and urea dosing conditions.[10, 11] An SCR system is temperature dependent for two reasons; one being that urea requires a minimum of 200 °C for thermalization to form ammonia needed for NO_x reduction, and two, the SCRs' catalyst is required to be above this temperature, depending on the material, to effectively reduce NO_x to N_2 due to the higher activation barrier for nitric oxide (NO).[12, 13] Current in-use systems have been able to comply with the laboratory certification testing, but it is debated how well the standards are actually met during on-road operations. Dixit et al. showed that low speed operations produce elevated NO_x emission factors, upwards of 2-4 times the certification levels due to lower engine operating temperatures, and the lowest emissions factors were achieved at higher operating temperatures.[14] Similarly, Quiros et al.

researched seven HDVs (five of which were diesels) and revealed that on-road HDVs in urban driving conditions and drayage operations tend to exceed the current NO_x standard.[15]

It is likely impossible to eliminate all engine out particles from combustion engines and so the current approach has been to trap the particles before they enter the atmosphere. Therefore, DPFs have been exclusively employed to meet the lower particle emission standards. DPFs are ceramic monolithic filters that work by way of interception and are effective at reducing particle emissions by more than 90 percent from pre-DPF levels filtering out all but the smallest of nanoparticles.[16-19]

In 2000, the California Air Resources Board instituted the California Diesel Risk Reduction Plan with the goal of reducing diesel PM emissions 85% statewide by 2020.[20] A variety of rules and regulations has encouraged the retirement of older HDVs and accelerated the penetration of lower emitting HDVs. To reduce the particle pollution in the San Pedro Port area, the San Pedro Bay Ports Clean Air Action Plan required all vehicles operating within the Ports of Los Angeles and Long Beach to have 2007 and newer engines equipped with DPFs resulting in a complete turnover of the Port fleet in 2010. [21, 22] The mandatory introduction of DPFs, seen in chassis model year 2008 and newer, has resulted in measurable reductions in the PM emissions from HDVs servicing the Los Angeles and Long Beach Ports.[17, 19, 21, 23] Statewide, the California Truck and Bus Rule established a time schedule for requiring all HDVs to meet these PM and NO_x standards. This rule requires older model year vehicles operating in California to either be replaced or comply with PM filter requirements as of January 1, 2015.[21,24] In addition, all trucks operating in California by 2023 must comply with both the 0.01 g/bhp-hr PM standard and 0.2 g/bhp-hr NO_x standard.

To track the accelerated turnover of California HDV fleets and to assess the progress made toward reaching the anticipated 85% PM emission reduction by 2020, emission measurements have been collected at two California HDV sites. These two sites are located at the Port of Los Angeles and Cottonwood weigh station on I-5 in Cottonwood, CA (17 miles south of Redding, CA). The Port of Los Angeles fleet is generally comprised of local HDVs with first generation DPFs that are involved in primarily short haul activities and has been slow to introduce SCR equipped HDVs. The Cottonwood weigh station fleet consists of interstate HDVs that are predominantly involved in long-haul operations. These contrasting fleets and retirement schedules have established different dynamics in the emission trends observed. This research adds a third in-use emissions data set to the measurements previously collected in 2013 and 2015 to form one of the largest in-use emissions database for HDVs.[25, 26] We have used this data set to compare and contrast these California fleet emission trends and examine the in-use effectiveness of the new after-treatment systems.

Experimental

Three successful campaigns in California have utilized the University of Denver's On-road Heavy-duty Measurement System (OHMS), with the setup and instrumentation detailed at length previously.[25] To summarize, HDVs drive under a 4.6 meter high and 15.2 meter long event tent, with a ceiling-mounted perforated polyethylene pipe that spans the length of the tent. Exhaust plumes from HDVs with elevated exhaust pipes are contained in the tent, and sampled through the polyethylene pipe which integrates the plume over the length of the tent as the HDV drives through. A portion of the exhaust plume is then drawn to the end of the polyethylene pipe by an end-mounted fan enabling a rapid fuel specific HDV emission measurement. Ground level exhaust HDVs are rarely measured, albeit an occasional ground level liquefied natural gas

(LNG) vehicles at the Port is measured due to high exhaust temperatures that elevates the exhaust plume quickly enough to be captured.

OHMS collects data on multiple gases through a twin piston diaphragm pump (KNF Neuberger, Inc. UN035.1.2ANP, 55 L/min), using ¼ inch Teflon tubing and a water condensation trap. The samples are analyzed using a Horiba AIA-240 non-dispersive infrared (IR) analyzer for carbon dioxide (CO_2) and carbon monoxide (CO), a Horiba FCA-240 that collects data on total hydrocarbons (HC) using a flame ionization detector and NO via ozone chemiluminescence, and a second Horiba FCA-240 measures total NO_x, also by ozone chemiluminescence and nitrogen dioxide (NO_2) is determined by the NO and NO_x difference. A Dekati Mass Monitor (DMM-230A, 0-1.2µm) measures total PM mass and particle number concentration ([PN]) with a cascading impactor. BC mass is measured by a Droplet Measurement Technologies photoacoustic extinctiometer (PAX 0-1µm) that uses photoacoustic absorption at 870 nm. These individual particle instruments use ¼ inch copper tubing to sample the exhaust. A fast mobility particle sizer (model 3091, FMPS, TSI Inc.) was used in the 2015 and 2017 campaigns to monitor fuel specific particle size distributions on individual HDVs for particles 5.6 to 560 nm.

The maximum span for the CO_2 analyzer was set at each site using a certified mixture of 3.5% CO_2 in nitrogen (Praxair). The gaseous analyzers were calibrated at the beginning and end of each day on location by injecting into the sample line, prior to the exhaust fan, a Bar-97 certified low-range calibration gas (0.5% CO, 6% CO_2, 200 ppm propane, and 300 ppm of NO in nitrogen). All species were divided by CO_2 to get an emission species to CO_2 ratio, which were averaged and divided by the certified bottle ratios to give scaling factors applied to each fuel specific HDV measurement for CO/CO_2, HC/CO_2, NO/CO_2 and NO_x/CO_2. The Dekati DMM-230A was factory calibrated and calibration of the PAX was performed in-lab prior to field measurements following the manufacturer's instructions. Both particle instruments were zero corrected daily as needed.

The analysis of exhaust plumes is initiated when a HDV exits OHMS triggering an IR body sensor. 15 seconds of data are then collected from all analyzers at 1 Hz. An increase of 75 ppm of CO_2 or more above background is required for a plume to be valid and all plumes are visually post-processed to ensure only one plume comprises each record. Both criterion must be met otherwise the measurement is rendered invalid and excluded from the results. Speed and acceleration at the entrance and exit of the tent are obtained from a pair of optical speed measurement bars.

Three separate cameras were used to image individual HDV license plates (important to attain non-personal vehicle identification information such as vehicle identification number, make and model year), visible blue caps on the driver side of the HDV, which indicates the presence of a urea tank needed for SCR systems, and an IR camera (Thermovision A20, Flir Systems) captures IR thermographs of the exhaust pipes for temperature determination. IR thermographs of the HDV exhaust pipes were converted into temperature (ºC) using an emissivity calibration curve defined from a previous field calibration.[25] License plate information for the 2017 measurements was matched against state records as well as an online reverse-plate lookup (www.searchquarry.com). HDV emission regulations are enforced based on engine manufacture year; however, the information acquired from a license plate only reveals chassis manufacture year. Our experience has shown that the chassis model year is almost always one model year newer than the engine and this assumption will be used for the subsequent analyses. Therefore, it is assumed that 2008 chassis model year and newer vehicles are manufactured to meet the 0.01 g/bhp-hr PM standard. Because NO_x emission standards have been phased-in, not all 2011 and newer chassis model year vehicles have been manufactured to meet these new standards. The proportion of HDVs meeting the standard has increased each year since 2011 but has yet to reach 100% of production, meaning an increasing number of 2011 and newer model year HDVs are equipped with SCR systems that meet the 0.2 g/bhp-hr.[6, 7]

The gases and particle measured ratios for each species were converted into fuel specific emissions of grams of pollutant per kilogram of fuel (g/kg of fuel) by carbon balance. For diesel HDVs a carbon mass fraction of 0.86 was used and for LNG fueled HDVs 0.75 was used.[27] The [PN] were post-processed to obtain fuel specific PN/kg of fuel data, as well as the FMPS data to acquire fuel specific PN emissions distributions by particle size bin.

This measurement setup collected fuel specific emissions at two California locations in three biennial years: 2013, 2015 and 2017. One location was at the Port of Los Angeles, managed by TRAPAC Inc. The OHMS tent was set up at the exit all three years, though the physical location of the exit changed between 2013 and 2015 as previously reported.[25] In 2017 the site was furthered altered with the addition of a speed bump just outside of the exit gate, reducing the number of valid measurements. The HDV fleet at the Cottonwood weigh station comprised the second fleet measured during these campaigns, and the measurement location went unchanged for all measurement years.

Results and Discussion

On-road fuel specific emission factors were collected at the Port of Los Angeles (795 measurements) and Cottonwood Weigh Station (1045 measurements) in the spring of 2017 adding to the 2013 and 2015 data sets, with that data shown in Table S1 and previously reported.[25, 26] All data sets are comprised of vehicles with a gross vehicle class weight rating of 7 and 8. Vehicles are not weighed at the Port, and although HDVs are subject to weigh station activities at Cottonwood, that information is not available. The Port fleet is entirely comprised of vehicles 2007 and newer and is a completely DPF equipped fleet while currently only 89% of the Cottonwood fleet is model year 2007 or newer. Table 1 summarizes the 2017 measurements with model year averages, number of measurements, unique vehicles, fleet average fuel specific emissions for CO, HC, NO, NO_2, NO_x, PM, BC, and PN, as well as entrance and exit speed and acceleration and IR exhaust temperature. Uncertainties are standard errors of the mean calculated using the distribution of the daily means (see Supporting Information). Diesel vehicles dominate the 2017 fleet with only 6 vehicles measured at the Port powered by LNG (3 lean burn with elevated exhaust and 3 stoichiometric combustion with ground level exhaust), and because of the negligible impact on the overall means, they have been included in the fleet averages.

The fleet at the Port of Los Angeles has continued to age in 2017 (7.5 years old) being 1.5 years older than the 2015 fleet (6 years old) and 3.3 years older than in 2013 (4.2 years old). 75% of the measurements are still comprised of vehicles older than model year 2011 with 2008 - 2009 model year vehicles contributing the largest number of measurements (57%). Traditionally drayage fleets have employed the oldest and lowest cost vehicles for these short haul operations. With the required fleet turn over in 2010 to DPF equipped HDVs, the Los Angeles and Long Beach Port fleet became the newest fleet in California. However, this fleet appears to be returning to previous operations where older vehicles that continue to age are the norm and few newer vehicles with improved aftertreatment systems are incorporated into the fleet. In contrast, the Cottonwood fleet continues to benefit from fleet turnover, induced by the California Truck and Bus rule, and is overall 1.8 model years newer in 2017 than observed in 2013, and is now 1.5

Table 1. Location, date, road grade, number of HDVs measured, average model year, mean fuel specific emissions (g/kg of fuel), with standard errors of the mean, speeds, accelerations and IR exhaust temperature.

Location/ Date/ Road grade	HDVs (Unique) mean MY	gCO/kg	gHC/kg	gNO^a/kg, gNO_2/kg, $gNO_x{}^b/kg$	gPM/kg	gBC/kg	PN/kg	Entrance/Exit Speed[c] Acceleration[d]	IR exhaust temp (°C)
Port of LA/ April 3-7 2017/ 0°	795 (628) 2009.8	1.7 ± 0.3	0.41 ± 0.08	14.6 ± 0.2, 3.7 ± 0.3, 27.6 ± 0.4	0.035 ± 0.01	0.03 ± 0.01	2.2×10^{14} $\pm 2.6 \times 10^{13}$	8.5/7.2 0.31/-0.68	86 ± 3
Cottonwood/ April 10-14 2017 / -0.5°	1045 (971) 2011.3	2.8 ± 0.4	0.28 ± 0.04	9.6 ± 0.7, 2.9 ± 0.1, 18.6 ± 1.2	0.09 ± 0.005	0.06 ± 0.003	7.7×10^{14} $\pm 9.5 \times 10^{13}$	11.3/11.9 0.23/0.16	108 ± 3

[a] grams of NO [b] grams of NO_2 [c] kilometers per hour [d] kilometers per hour per second

years newer than the Port of Los Angeles fleet. 62% of the 2017 Cottonwood fleet is model year 2011 and newer compared to only 25% at the Port.

Oxides of Nitrogen

Figure 1 shows the five year emission trends at both locations for all gaseous emissions. 2013 (grey), 2015 (green) and 2017 (red) are shown for CO (solid), HC (triangles), NO (moles of NO, open), NO_2 (horizontal striped) and NO_x (moles of NO_2, hatched) at the Port of Los Angeles and Cottonwood. A 26% increase at the Port and a 16% decrease at Cottonwood in fleet average NO_x emissions, mainly NO, from 2015 to 2017 data were the only gaseous emission with a statistically significant change (validated with a null hypothesis test at the 95% confidence level). The NO_x fleet average in 2017 (27.6 gNO_x/kg of fuel) at the Port of Los Angeles is a significant increase from the means observed in 2013 and 2015 (20.7 and 21.6 gNO_x/kg of fuel respectively). The Port and Cottonwood have similar 2008-2010 model year average NO_x emissions (30.0 ± 0.5 and 27.4 ± 1.0 respectively) and both show increases with age (see Supporting Information Figures S1 and S2).

Overall, fleet average fuel specific NO_x emissions at Cottonwood are now 33% lower than at the Port. Figure 2 graphs the 2017 fuel specific NO_x emissions as a function of model year for the Port of Los Angeles (grey) and Cottonwood (red) data. NO is displayed as grams of NO_2 (solid and hatched bars) along with NO_2 (open bars) so the height of the bar is total gNO_x/kg of fuel by model year. Uncertainties are standard errors of the mean calculated using the daily means. A third of the difference is due to the fact that the newest model years plotted in Figure 2 at Cottonwood have lower fuel specific NO_x emissions. The Port data is noisier due to a smaller number of 2011 and newer vehicles in the fleet but does not show the same systematic NO_x

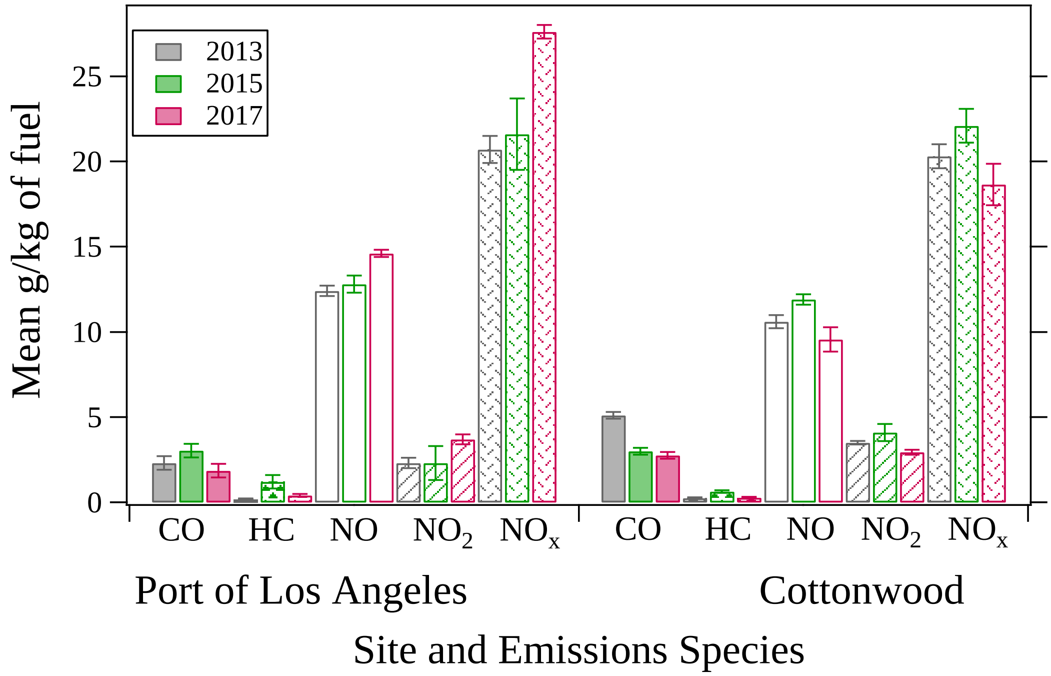

Figure 1. 2013 (grey-left bars), 2015 (green-middle bars) and 2017 (red-right bars) data from the Port of Los Angeles (left) and Cottonwood (right) for CO (solid), HC (triangles), NO (open), NO_2 (horizontal stripes) and NO_x (hatched) gases. Uncertainties are standard error of the means calculated using the daily means.

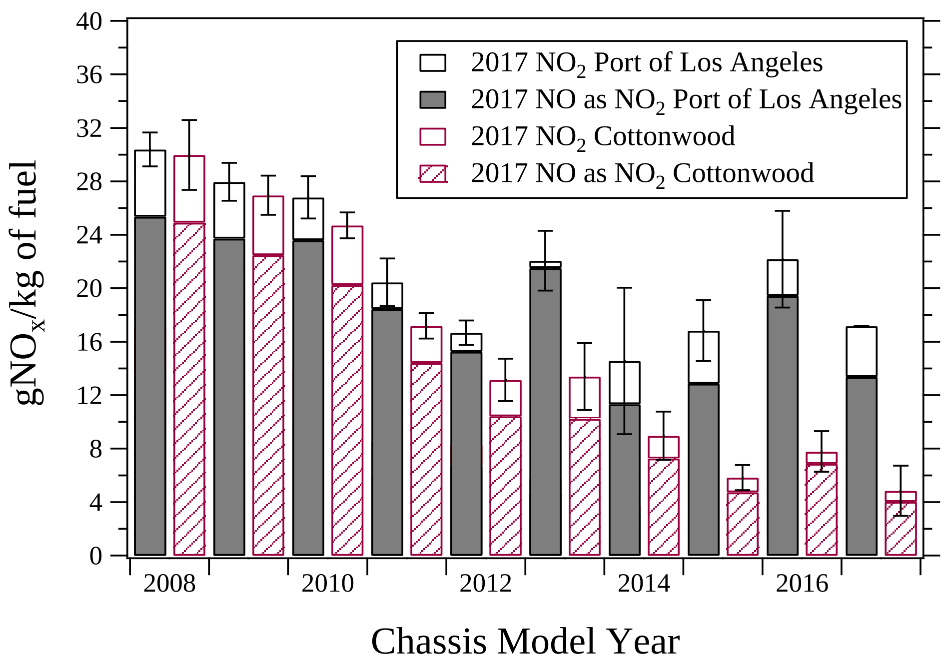

Figure 2. Total fuel specific NO_x emissions by model year for the Port of Los Angeles (grey-left bars) and Cottonwood (red-right bars). Filled/hatched portions are gNO/kg of fuel as NO_2 equivalents and open portions are NO_2. Uncertainties are standard errors of the mean calculated using the daily means of the total NO_x.

reductions with model year as observed at Cottonwood. To emphasize this point, average NO_x emissions for model years 2011 and newer at the Port of Los Angeles were 20.1 ± 0.9 gNO_x/kg of fuel, compared to 10.6 ± 1.2 gNO_x/kg of fuel at Cottonwood. Even after age adjusting the Port of Los Angeles 2011 and newer fleet to match that of Cottonwood, the mean fuel specific NO_x emissions of the Port fleet changed little (20.1 to 19.6 gNO_x/kg of fuel) again demonstrating the lack of a NO_x model year dependence at the Port. The remaining NO_x difference is simply due to a higher percentage of 2011 and newer HDVs at Cottonwood. Figure S3 in the Supporting Information shows that the fleet fraction of vehicles at Cottonwood has shifted since 2013 to a higher percentage of vehicles model year 2011 and newer.

Proper SCR function relies on temperatures hot enough to thermalize urea (typically a minimum of 200 ºC prior to the catalyst) in addition to a catalyst temperature that lowers the activation barrier to successfully reduce NO_x. As reported by others, HDVs subject to drayage driving modes have been found to have lower average engine temperatures, problematic for current SCR systems.[15, 28] Table 1 shows that the average IR exhaust pipe temperature observed at Cottonwood is considerably higher than at the Port of Los Angeles. If the comparison is restricted to vehicles model year 2011 and newer, the difference increases to 110 ºC and 79 ºC (t-test, greater than 99% confidence). This temperature difference is likely the major factor in the difference in observed NO_x emissions for the newest model year HDVs at each location. The lack of any meaningful decrease in NO_x, especially NO_2 emissions, for the newer model years at the Port of Los Angeles supports other reports that the activity cycle for a majority of the HDVs at the Port is insufficient to consistently support active SCR systems.[15, 29]

The reduction observed at Cottonwood is a result of a newer fleet having an increasing percentage of low emitting NO_x HDVs than at the Port, indicating the SCRs at Cottonwood are more effective likely due to elevated operating temperatures. As the California Truck and Bus rule forces the early retirement of pre-SCR HDVs, there is an expectation that the NO_x emissions will continue to decrease in the Cottonwood fleet. Using the 2017 and newer model year average emissions (~4.7 gNO_x/kg of fuel), a factor of 4 reduction is possible from the current fleet average. While HDV SCR systems are not expected to perform at optimum levels in a weigh station, the observations at both locations strongly suggest that current on-road HDV NO_x emissions are higher than the certification standards.

Particulate Matter

The PM reduction story is more consistent between these two sites and parallels other observations of dramatic reductions in diesel PM with the introduction of DPFs.[17, 30] Overall fleet average emissions for the Port of Los Angeles (left) and Cottonwood (right) for 2013 (grey), 2015 (green) and 2017 (red) measurement years are displayed in Figure 3. Fuel specific PM (solid bars) and BC (hatched bars) are plotted against the left axis and fuel specific PN (open bars) are shown against the right axis. Uncertainties are standard errors of the mean calculated using the daily means. The averages from the Port of Los Angeles have been consistently lower than the Cottonwood fleet, a result stemming from all vehicles at the Port having DPFs installed since 2010. The BC and PN means are significantly lower than similar observations from the Port of Oakland, though the emission trends are consistent. Reported literature values support the lower values. While the reasons for these discrepancies are unknown, the possibilities have been extensively discussed in a previous publication.[25]

In 2015 there were significant increases at the Port for all three particle species, as there was an increase in the fraction of higher emitting HDVs. The 2015 fleet PM, BC and PN increased from

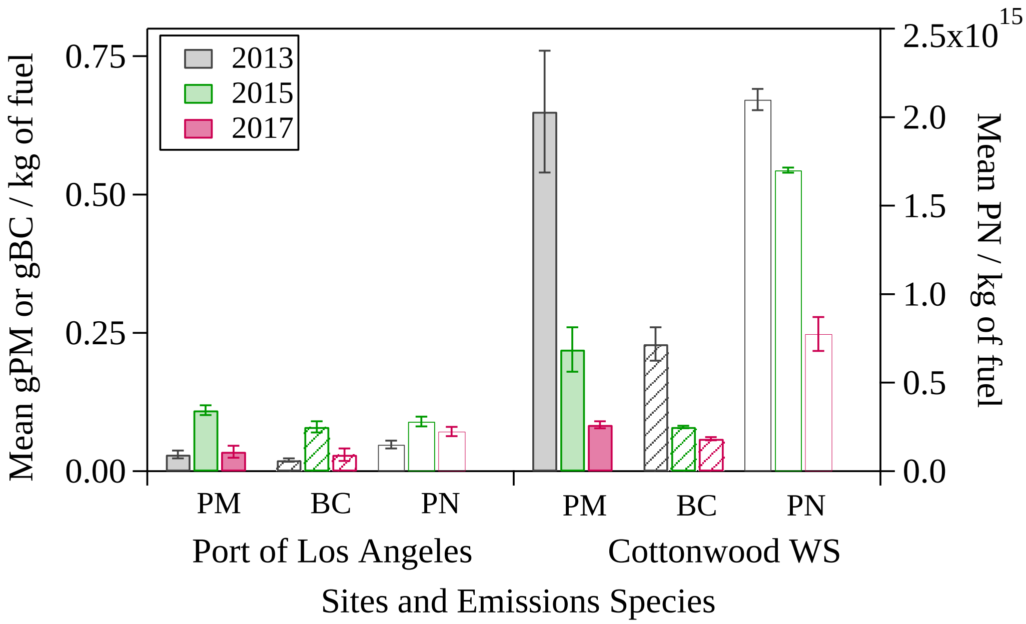

Figure 3. Fuel specific mean emissions for PM (solid, left axis), BC (diagonal, left axis) and PN (open, right axis) at the Port of Los Angeles and Cottonwood Weigh Station for 2013 (grey-left bar), 2015 (green-middle bar) and 2017 (red-right bar) HDV fleets. Uncertainties are standard errors of the mean calculated using the daily means.

the 2013 data by +266%, +300% and +87% respectively. High emitting HDVs were found in model years 2008-2010 and were responsible for this increase (see Figure S4). These model years possess engines that trade higher engine out PM emissions for NO_x control and therefore rely heavily on the functionality of a properly working DPFs in order to limit tailpipe PM emissions.[31] In 2017 the removal and or repair of these vehicles accounts for the decrease in particle emissions and a return to near 2013 levels (63% reduction from 2015 PM and BC levels). In particular, a single 2009 vehicle measured in 2015 was responsible for over 40% of the cumulative PM and 47% of BC. When measured in 2017 it was found to be low emitting and accounts for a majority of the reductions observed. The emissions distribution at the Port of Los Angeles is still more skewed than observed in 2013 (see Figure S6 in the Supporting Information) indicating the remaining presence of HDVs with DPF problems, though much less so than observed in 2015.

The 2013 fuel specific particle emission averages at Cottonwood were significantly higher than at the Port (see Figure 3) due to it being an older, less regulated fleet with more pre-DPF engines. The 2015 measurements showed decreases from the 2013 data (PM -66%, BC -65% and PN -19%) in response to newer vehicles being added to the fleet and older vehicles being retrofit with DPFs, decommissioned or relocated.[25] Previous behaviors continued to lower emissions in the 2017 fleet leading to an additional PM, BC and PN decreases of -60%, -25% and -55% respectively from 2015 data. The PM and BC levels at Cottonwood are now comparable to the levels found with a fully DPF fleet observed at the Port of Los Angeles. The overall reduction of 87% of PM from 2013 to 2017 for the Cottonwood fleet is three years ahead of the goal set in the Diesel Risk Reduction Plan by the California Air Resources Board.[20]

Cottonwood particle emissions have been positively impacted through the shift to newer model year vehicles and retrofit activity among remaining older model year vehicles. Contributions from each model year at Cottonwood are shown in Figure 4 for (a) mean fuel specific BC by model year, (b) fleet percentage by model year, and (c) the percent contribution for each model year, assuming equal vehicle fuel consumption, to the total BC emissions for 2013 (black) and 2017 (red) data. Uncertainties are standard errors of the mean calculated using the daily means, and vehicles model year 2000 and older have been combined. All particle emissions in the remaining older model year vehicles have undergone significant BC decreases as retrofits have been installed.[25] The large decrease between model year 2007 and 2008 coincides with the introduction of vehicles originally equipped with DPFs.

Vehicles model year 2007 and older comprised 61% of the fleet measured in 2013 (Figure 4b), but only 13% of the 2017 fleet; the highest individual fleet percentage in 2013 came from vehicles that were older than model year 2001 (more than 20%). These vehicles also dominated

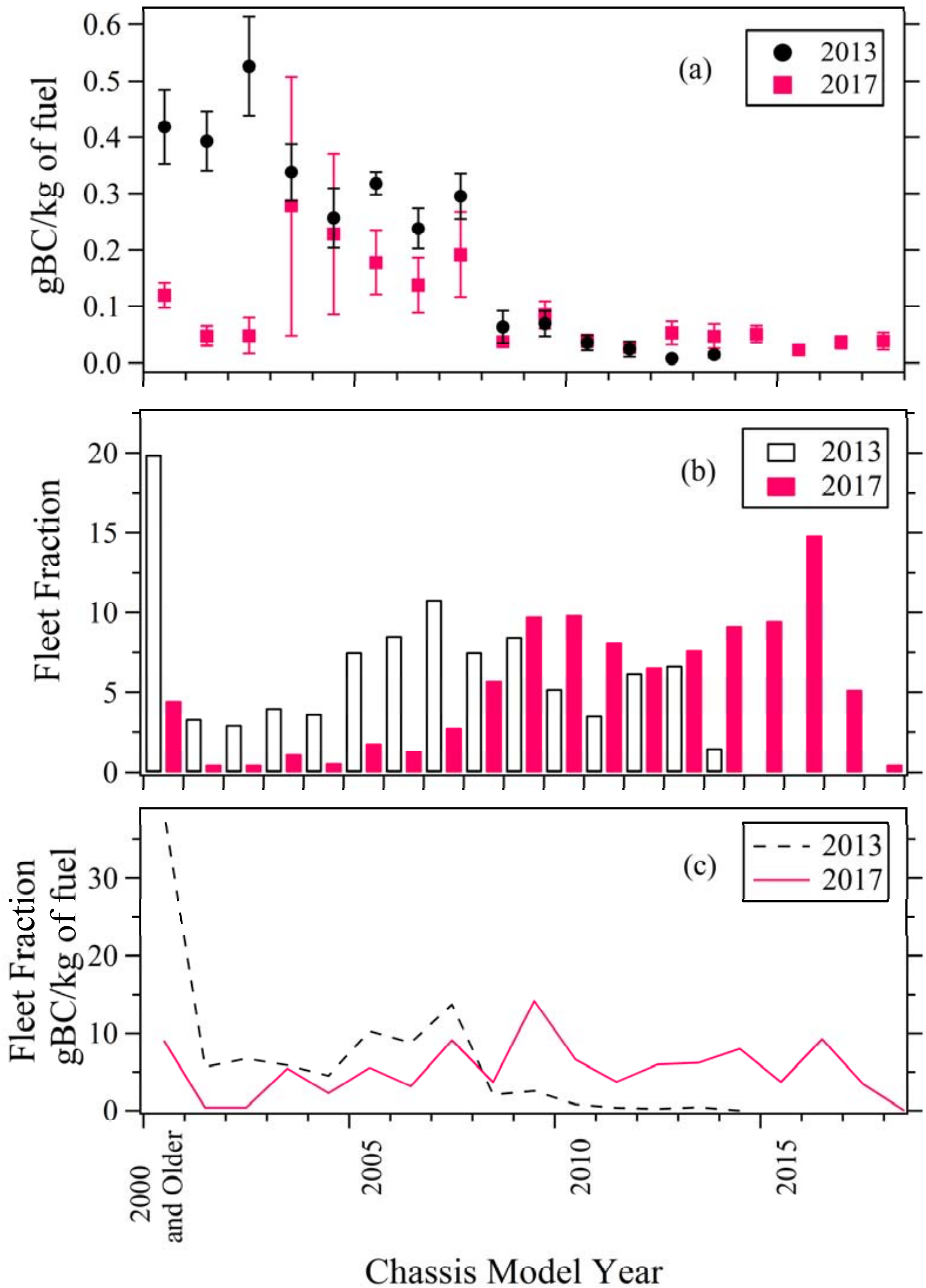

Figure 4. 2013 and 2017 (a) mean fuel specific black carbon emissions (b) fleet percentages and (c) fleet percent contribution, assuming equal vehicle fuel consumption, all versus model year. Uncertainties are standard errors of the mean calculated using the daily means.

the BC total percent contribution (Figure 4c) while model year 2010 and newer were a minor contribution to the overall total in 2013. HDVs with retrofits are evident in Figure 4b, as older model years have reduced gBC/kg of fuel average in 2017 compared to 2013. In 2017 the newest model year vehicles are now responsible for the majority of the overall BC emissions but those percentage contributions are for a fleet total which has undergone a factor of 7 reduction between 2013 and 2017. The five year reductions observed at Cottonwood illustrate the effectiveness of the new technology and how the California Truck and Bus Rule is making an impact at lowering the on-road particulate emissions inventory in California.

As the particle emissions at Cottonwood have steadily decreased, the fleet averages are now dominated by a few high emitting vehicles. Figure 5 shows the fuel specific PM distribution versus fleet fraction at the Cottonwood weigh station for 2013 (black dotted line), 2015 (blue dashed line) and 2017 (red solid line) data. The 1:1 line would be representative of each HDV in the fleet contributing equally to the overall fleet averages, and deviation from this ratio indicates a more skewed emissions distribution. In 2013, half of the PM emissions were from 12% of the measurements, and in 2017 half of the PM emissions were from 5.5% of the measurements. This is the result of not just newer HDVs being added to the fleet but a majority of the older vehicles that remain in the Cottonwood fleet having lower emissions both contributing to improved fleet emissions over the years.

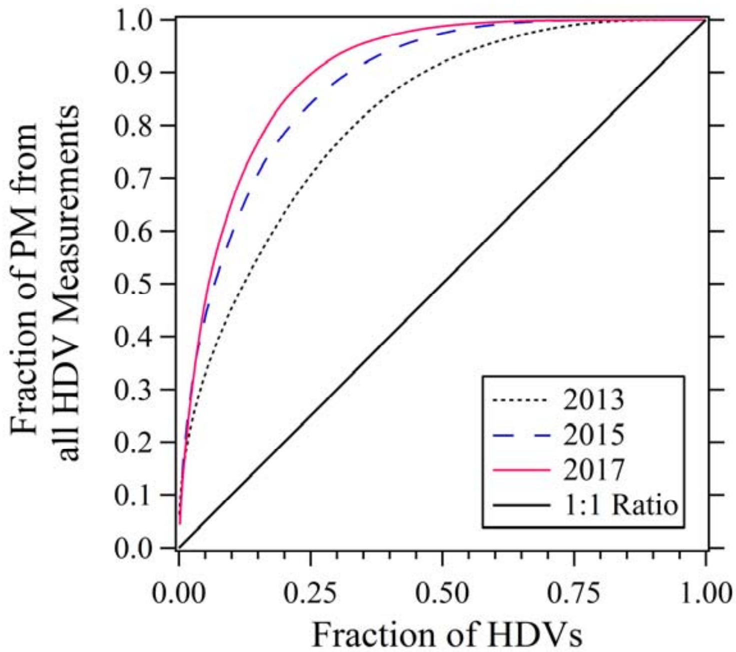

Figure 5. Fraction of HDVs responsible for the fraction of fuel specific PM from all HDV measurements at Cottonwood shown for 2013 (dotted black line), 2015 (dashed blue line) and 2017 (solid red line). The solid black line represents the 1:1 ratio.

Supporting Information. Supporting figures (S1-S6) and table (ST1) referenced in the text. This material is available free of charge at http://pubs.acs.org

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): G. A. Bishop acknowledges receipt of patent royalty payments from Envirotest, an operating subsidiary of Opus Inspection, which licenses vehicle emissions testing technology developed at the University of Denver.

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REFERENCES

1. Health Effects Institute *Traffic-related Air Pollution: A Critical Review of the Literature on Emissions, Exposure, and Health Effects. A Special Report of the HEI Panel of the Health Effects of Traffic-related Air Pollution*; 2010.

2. International Agency for Research on Cancer IARC: Diesel engine exhaust carcinogenic. Press Release 213. http://www.iarc.fr/en/media-centre/pr/2012/pdfs/pr213_E.pdf (Aug. 2016),

3. Office of Environmental Health Hazard Assessment; California Environmental Protection Agency *Part B: Health risk assessment for diesel exhaust*; Sacramento, 1998.

4. California Air Resources Board *Risk Reduction Plan to Reduce Particulate Matter Emissions from Diesel-fueled Engines and Vehicles*; Sacramento, CA, 2000.

5. California Code of Regulations, Regulation to reduce emissions of diesel particulate matter, oxides of nitrogen and other criteria pollutants, from in-use heavy-duty diesel-fueled vehicles. In *Title 13*, 2008.

6. Code of Federal Regulations, NO_x and particulate averaging, trading and banking for heavy-duty engines. In *Title 40*, 2001; vol. 12, pp 7, 215-290.

7. Code of Federal Regulations, NO_x plus NMHC and particulate averaging, trading and banking for heavy-duty engines. In *Title 40*, 2000; vol. 10, pp 7-169.

8. Code of Federal Regulations, Emission standards and supplemental requirements for 2007 and later model year diesel heavy-duty engines and vehicles. In *Title 40* 2008.

9. U.S. Environmental Protection Agency, The Clean Air Act. In 2004.

10. Gekas, I.; Vressner, A.; Johansen, K. NOx reduction potential of V-SCR catalyst in SCR/DOC/DPF configuration targeting Euro VI limits from high engine NOx levels. *SAE International* **2009**.

11. Manufacturers of Emission Controls Association, Emission Control Technologies for Diesel-Powered Vehicles. In 2007; p 28.

12. Koebel, M.; Elsener, M.; Kleemann, M. Urea-SCR: a promising technique to reduce NO_x emissions from automotive diesel engines. *Catal. Today* **2000,** 59, 335-345.

13. Smirniotis, P. G.; Peña, D. A.; Uphade, B. S. Low-temperature selective catalytic reduction (SCR) of NO with NH_3 by using Mn, Cr, and Cu oxides supported on Hombikat TiO_2. *Angew. Chem. Int. Ed.* **2001,** 40, (13), 2479-2482.

14. Dixit, P.; Miller, J. W.; III, D. R. C.; Oshinuga, A.; Jiang, Y.; Durbin, T. D.; Johnson, K. C. Differences between emissions measured in urban driving and certification testing of heavy-duty diesel engines. *Atmos. Environ.* **2017,** 166, 276-285.

15. Quiros, D. C.; Thiruvengadam, A.; Pradhan, S.; Besch, M.; Thiruvengadam, P.; Dermirgok, B.; Carder, D.; Oshinuga, A.; Huai, T.; Hu, S. Real-world emissions from modern heavy-duty diesel, natural gas, and hybrid diesel trucks operating along major California freight corridors. *Emiss. Control Sci. Technol.* **2016,** 2, 156-172.

16. Bishop, G. A.; Schuchmann, B. G.; Stedman, D. H.; Lawson, D. R. Emission changes resulting from the San Pedro Bay, California Ports Truck Retirement Program. *Environ. Sci. Technol.* **2012,** 46, 551-558.

17. Preble, C. V.; Dallmann, T. R.; Kreisberg, N. M.; Hering, S. V.; Harley, R. A.; Kirchstetter, T. W. Effects of particle filters and selective catalytic reduction on heavy-duty diesel drayage truck emissions at the Port of Oakland. *Environ. Sci. Technol.* **2015,** 49, (14), 8864-8871.

18. Herner, J. D.; Hu, S.; Robertson, W. H.; Huai, T.; Collins, J. F.; Dwyer, H.; Ayala, A. Effect of advanced aftertreatment for PM and NO_x control on heavy-duty diesel truck emissions. *Environ. Sci. Technol.* **2009,** 43, 5928-5933.

19. Kozawa, K. H.; Park, S. S.; Mara, S. L.; Herner, J. D. Verifying emission reductions from heavy-duty diesel trucks operating on Southern California freeways. *Environ. Sci. Technol.* **2014,** 48, (3), 1475-1483.

20. California Air Resources Board Risk reduction plan to reduce particulate matter emissions from diesel-fueled engines and vehicles. https://www.arb.ca.gov/diesel/documents/rrpFinal.pdf

21. Bishop, G. A.; Schuchmann, B. G.; Stedman, D. H. Heavy-duty truck emissions in the South Coast Air Basin of California. *Environ. Sci. Technol.* **2013,** 47, (16), 9523-9529.

22. Port of Long Beach; Port of Los Angeles San Pedro Bay Ports Clean Air Action Plan: About the Clean Air Action Plan. http://www.cleanairactionplan.org (Dec. 2016),

23. Dallmann, T. R.; Harley, R. A.; Kirchstetter, T. W. Effects of diesel particle filter retrofits and accelerated fleet turnover on drayage truck emissions at the Port of Oakland. *Environ. Sci. Technol.* **2011,** 45, 10773-10779.

24. California Air Resources Board Truck and Bus Regulation. https://www.arb.ca.gov/msprog/onrdiesel/onrdiesel.htm

25. Haugen, M. J.; Bishop, G. A. Repeat fuel specific emission measurements on two California heavy-duty truck fleets. *Environ. Sci. Technol.* **2017,** 51, 4100-4107.

26. Bishop, G. A.; Hottor-Raguindin, R.; Stedman, D. H.; McClintock, P.; Theobald, E.; Johnson, J. D.; Lee, D.-W.; Zietsman, J.; Misra, C. On-road heavy-duty vehicle emissions monitoring system. *Environ. Sci. Technol.* **2015,** 49, (3), 1639-1645.

27. Bishop, G. A. FEAT Math II. http://www.feat.biochem.du.edu/assets/reports/FEAT_Math_II.pdf (accessed December 2014),

28. Miller, W.; Johnson, K. C.; Durbin, T.; Dixit, P. *In-use emissions testing and demonstration of retrofit technology for control of on-road heavy-duty engines*; University of California CE-CERT: 2013; pp 89-92.

29. Thiruvengadam, A.; Besch, M. C.; Thiruvengadam, P.; Pradhan, S.; Carder, D.; Kappanna, H.; Gautam, M.; Oshinuga, A.; Hogo, H.; Miyasato, M. Emission rates of regulated pollutants from current technology heavy-duty diesel and natural gas goods movement vehicles. *Environ. Sci. Technol.* **2015,** 49, 5236-5244.

30. May, A. A.; Nguyen, N. T.; Presto, A. A.; Gordon, T. D.; Lipsky, E. M.; Karve, M.; Gutierrez, A.; Robertson, W. H.; Zhang, M.; Brandow, C.; Chang, O.; Chen, S.; Cicero-

Fernandez, P.; Dinkins, L.; Fuentes, M.; Huang, S.-M.; Ling, R.; Long, J.; Maddox, C.; Massetti, J.; McCauley, E.; Miguel, A.; Na, K.; Ong, R.; Pang, Y.; Rieger, P.; Sax, T.; Truong, T.; Vo, T.; Chattopadhyay, S.; Maldonado, H.; Maricq, M. M.; Robinson, A. L. Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles. *Atmos. Environ.* **2014,** 88, 247-260.

31. Bell, J., *Modern Diesel Technology: Electricity and Electronics*. 2 ed.; Cengage Learning: 2013.

Supporting Information For:

Long-Term Fuel-Specific NO_x and Particle Emission Trends for In-Use Heavy-Duty Vehicles in California

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Summary of Supporting Information:

8 pages (excluding cover):

Table

Table S1: Location, number of HDVs measured, average model year, mean fuel-specific emissions (g/kg of fuel), with standard errors of the mean calculated using the daily means, speeds, accelerations and IR exhaust temperature.

Figures

Figure S1: 2013 (gray circles), 2015 (green diamonds) and 2017 (red squares) data from the Port of Los Angeles gNO_x/kg of fuel versus chassis model year. Uncertainties are standard error of the means calculated using the daily means.

Figure S2: 2013 (black circles), 2015 (blue diamonds) and 2017 (red squares) data from the Cottonwood gNO_x/kg of fuel versus chassis model year. Uncertainties are standard error of the means calculated using the daily means.

Figure S3: Cottonwood (a) gNO_x/kg of fuel emissions percentage contribution to total NO_x for 2013 (black dashed line) and 2017 (solid blue line) and (b) fleet percentage versus model year for 2013 (black open bars and 2017 (blue solid bars) data.

Figure S4: gPM/kg of fuel by Chassis model year for 2013 (grey circles), 2015 (green diamonds) and 2017 (red squares) data at the Port of Los Angeles. Uncertainties are standard error of the mean calculated using the daily means.

Figure S5: gPM/kg of fuel by Chassis model year for 2013 (black circles), 2015 (blue diamonds) and 2017 (red squares) data at Cottonwood. Uncertainties are standard error of the mean calculated using the daily means.

Figure S6: Fraction of each HDV measurement responsible for the corresponding fraction of total PM at the Port of Los Angeles for 2013 (black dotted line), 2015 (green dashed line) and 2017 (solid red line) data. The solid black line represents the 1:1 ratio.

Estimation of Standard Errors of the Mean for Reported Uncertainties

Vehicle emissions from US vehicle fleets are not normally distributed, thus the assigning of uncertainties on fleet emission means involves a process that many readers may not be familiar with. Standard statistical methods that were developed for normally distributed populations, when used on a skewed distribution, result in uncertainties that are unrealistically too small due to the large number of samples. The Central Limit Theorem in general indicates that the means of multiple samples, randomly collected, from a larger parent population will be normally distributed, irrespective of the parent populations underlying distribution. Since we almost always collect multiple days of emission measurements from each site, we use these daily measurements as our randomly collected multiple samples from the larger population and report uncertainties based on their distribution. We calculate means, standard deviations and finally standard errors of the mean for this group of daily measurements. We report the fleet weighted means for all of the emission measurements and then calculate a standard error of this weighted mean by applying the same error percentage obtained from the ratio of the standard error of the mean for the daily measurements divided by the daily measurement mean. An example of this process is provided below for the 2015 Port of Los Angeles, CA gNO/kg of fuel and gPM/kg of fuel measurements. While this example is for a fleet mean we also use this technique when we report standard errors of the mean for individual model years or specific fuel or technology types. For example each model year will have its daily means averaged and then its standard error of the mean for the daily average computed and that percent uncertainty (STD Error MY/Daily MY average) will be applied to that model year's fleet mean emissions.

Cottonwood, CA 2017

Date	Mean gNO/kg of fuel	Counts	Mean gPM/kg of fuel	Counts
4/10/2017	9.5	318	0.08	325
4/11/2017	12.1	166	0.08	170
4/12/2017	8.2	183	0.09	190
4/13/2017	9.8	215	0.10	223
4/14/2017	8.1	134	0.08	137
Average for Daily Means	9.5		0.09	
Standard Error for the Daily Means	0.7		0.005	
Weighted Fleet Mean	9.6		0.09	
Standard Error for the Fleet Means	0.7		0.005	
As Reported in Table 1	9.6 ± 0.7		0.09 ± 0.005	

Table S1. Location, number of HDVs measured, average model year, mean fuel-specific emissions (g/kg of fuel), with standard errors of the mean calculated using the daily means, speeds, accelerations and IR exhaust temperature.

Location	HDVs mean MY	gCO/kg	gHC/kg	gNO[a]/kg gNO_2/kg gNO_x[b]/kg	gPM/kg	gBC/kg	PN/kg	Entrance/Exit Speed[c] Acceleration[d]	IR exhaust temp (ºC)
Port of LA 2013	1219 2009.1	2.3 ± 0.4	0.2 ± 0.03	12.4 ± 0.3 2.3 ± 0.3 20.7 ± 0.8	0.03 ± 0.01	0.02 ± 0.003	$1.5 \times 10^{14} \pm 2.5 \times 10^{13}$	7.7/9.3 0.3/0.5	86 ± 1
Port of LA 2015	1456 2009.3	3.0 ± 0.4	1.2 ± 0.4	12.8 ± 0.5 2.3 ± 1.0 21.6 ±2.1	0.11 ± 0.01	0.08 ± 0.01	$2.8 \times 10^{14} \pm 2.8 \times 10^{13}$	11.3/11.9 0.3/N.A.	91 ± 2
Cottonwood 2013	1866 2005.6	5.1 ± 0.2	0.3 ± 0.04	10.6 ± 0.4 3.5 ± 0.1 20.3 ± 0.7	0.64 ± 0.11	0.23 ± 0.03	$2.1 \times 10^{15} \pm 6.0 \times 10^{13}$	15.8/16.9 1.1/1.0	98 ± 5
Cottonwood 2015	694 2008.1	3.0 ± 0.2	0.7 ± 0.1	11.9 ± 0.2 4.1 ± 0.5 22.1 ± 0.7	0.22 ± 0.04	0.08 ± 0.002	$1.7 \times 10^{15} \pm 1.4 \times 10^{13}$	14.5/15.0 0.6/0.5	105 ± 1

[a] grams of NO [b] grams of NO_2 [c] kilometers per hour [d] kilometers per hour per second

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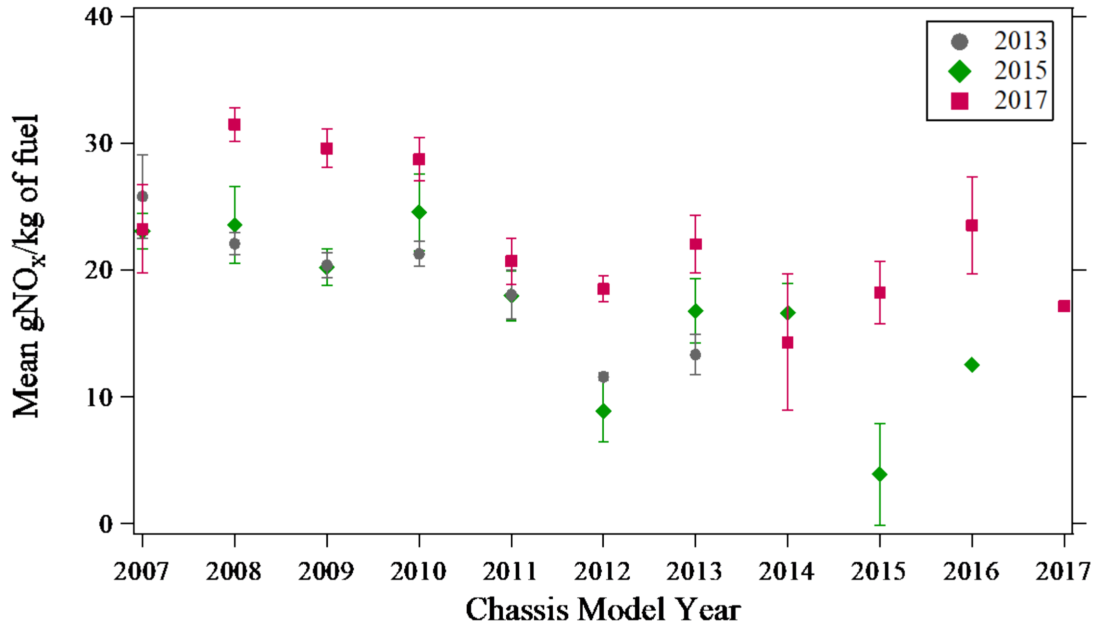

Figure S1. 2013 (gray circles), 2015 (green diamonds) and 2017 (red squares) data from the Port of Los Angeles gNO_x/kg of fuel versus chassis model year. Uncertainties are standard error of the means calculated using the daily means.

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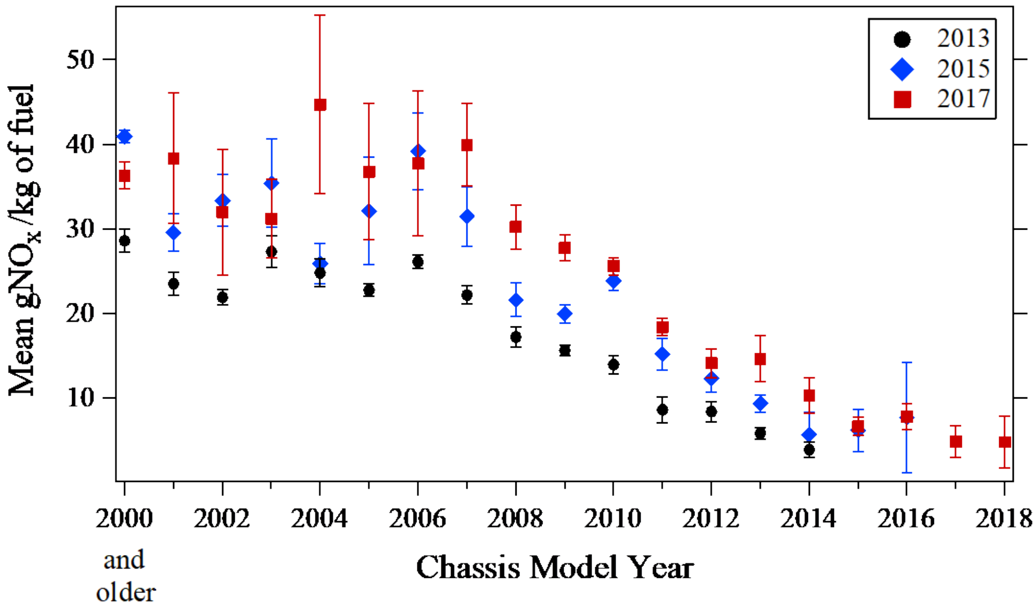

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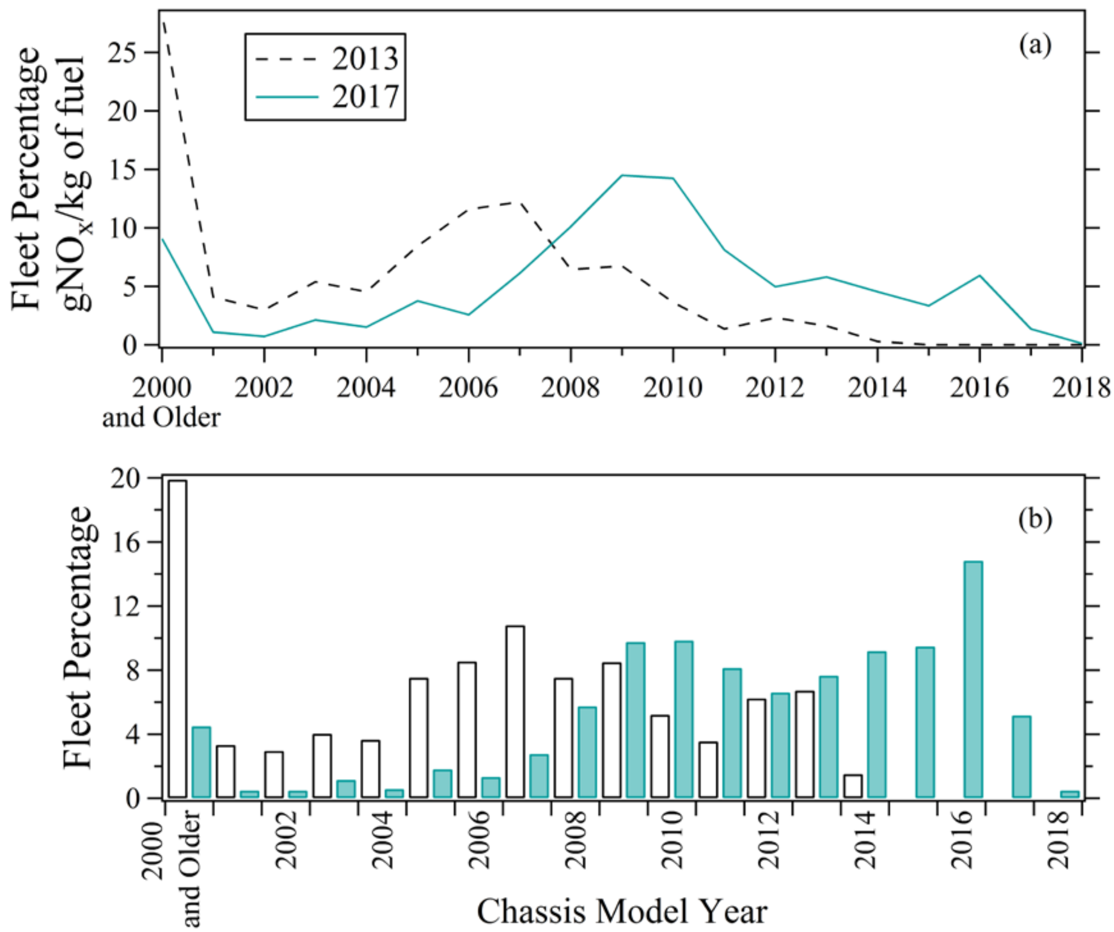

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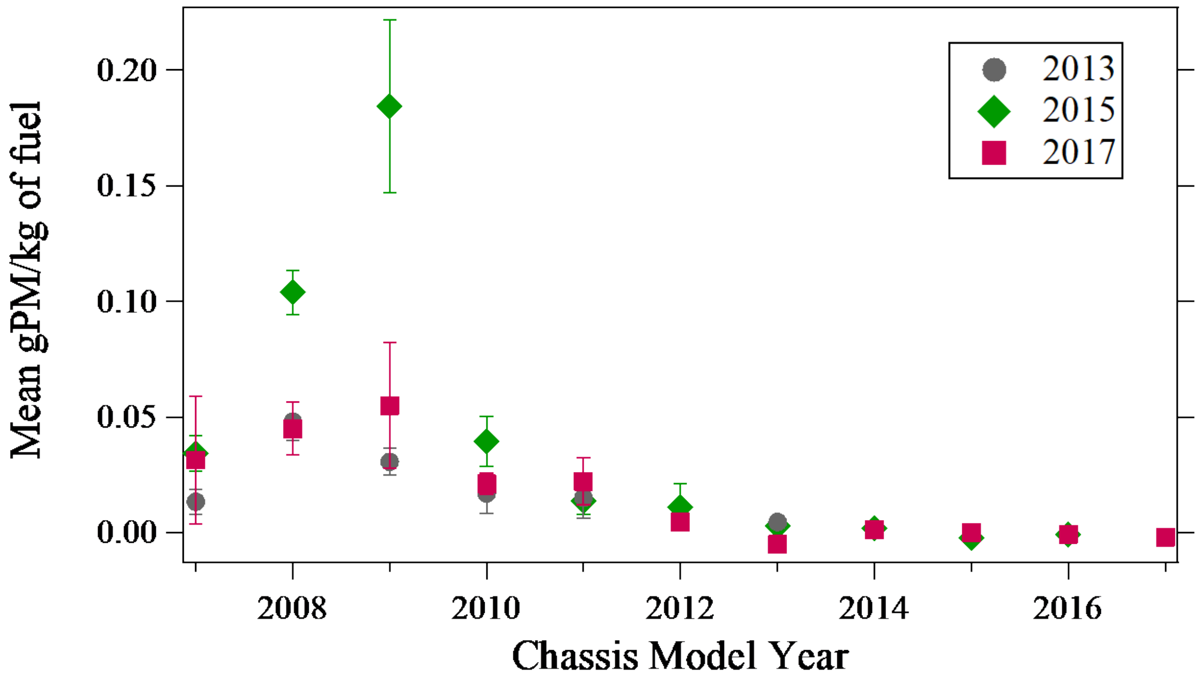

Figure S4. gPM/kg of fuel by Chassis model year for 2013 (grey circles), 2015 (green diamonds) and 2017 (red squares) data at the Port of Los Angeles. Uncertainties are standard error of the mean calculated using the daily means.

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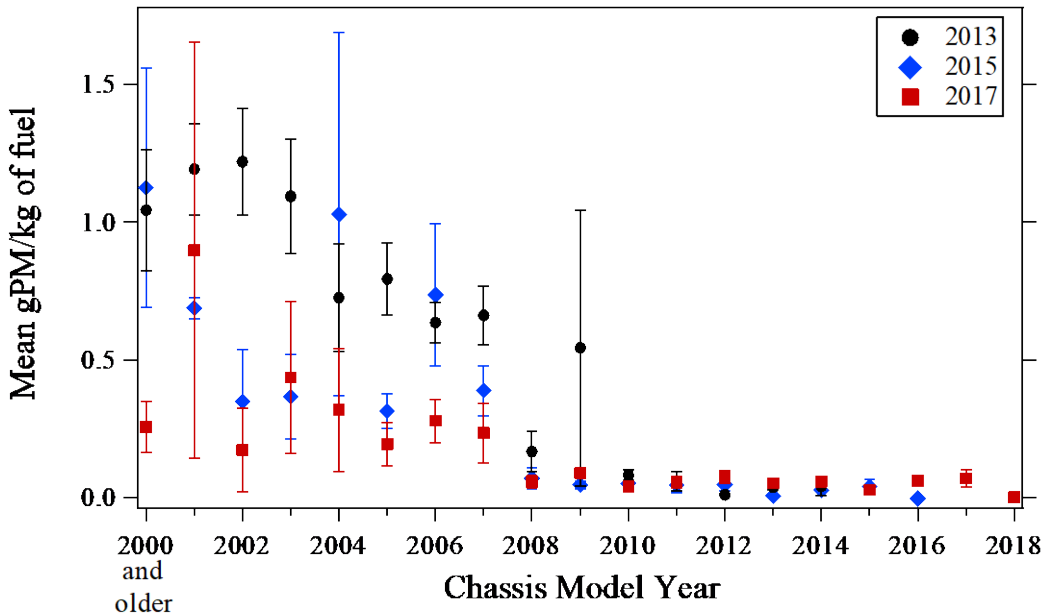

Figure S5. gPM/kg of fuel by Chassis model year for 2013 (black circles), 2015 (blue diamonds) and 2017 (red squares) data at Cottonwood. Uncertainties are standard error of the mean calculated using the daily means.

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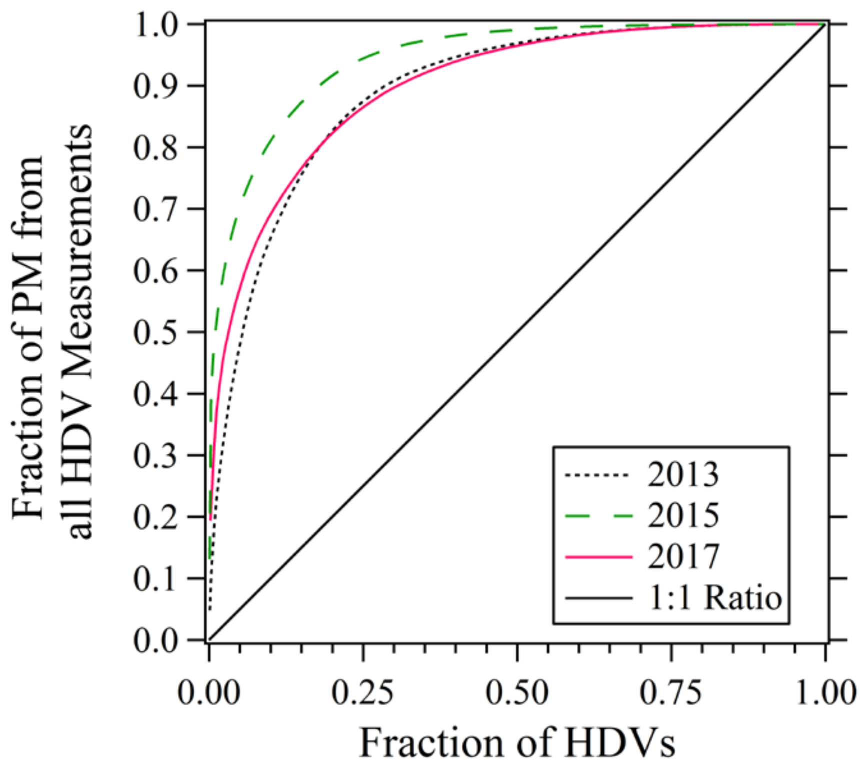

Figure S6. Fraction of each HDV measurement responsible for the corresponding fraction of total PM at the Port of Los Angeles for 2013 (black dotted line), 2015 (green dashed line) and 2017 (solid red line) data. The solid black line represents the 1:1 ratio.

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